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THE PRODUCTION OF SULPHURIC ACID FROM ALTERNATIVE SOURCES OF SULPHUR

by J.D. McFarlane and V. Robinson

1. Elemental sulphur from a technological point of view is a very attractive material for the manufacture of sulphuric acid. Plant costs are generally lower than for other materials, and design, and operation are easier. The most important source of this material is underground deposits mined by the well-known Frasch process which gives a very pure product but, unfortunately, for most developing countries, the main deposits are in the United States and Mexico with an increasing production in Poland. Likewise the largest production of sulphur recovered as a byproduct of refinery or natural gas processing operations is probably at Lacq in France, with substantial quantities from Canada and America; none of these places can be termed "less developed areas". There are also other sources of natural sulphur such as the Sicilian Mines which have been known and worked since classical times together with mines in other countries: such materials tend to be more expensive and rather less pure than the Frasch or recovered sulphur and many of them are not suitable for the simplest type of sulphur burning acid plant.

2. Iron pyrites is the major alternative to sulphur as a raw material for sulphuric acid production. This is much more widely distributed than sulphur and a large part of world production is based on it. Normal high quality material contains about 48% by weight of sulphur so that raw material transport costs have a greater effect on plant location and manufacturing costs than when using sulphur itself. Furthermore, the residues of iron oxide cinder left from the roasting process may not be suitable for charging to the blast furnace and may therefore present a disposal problem. At the present time in countries such as Britain without indigenous sources of sulphur or pyrites sulphuric acid can be produced at about the same price from either; this is because the opposing effects of transport costs and the residual value of cinder are approximately in balance. Any decline in the value of the cinder as steelworks raw material would make pyrites based acid appreciably more expensive. The latter is in any case true for many countries situated a long way from a pyrites source.

3. Other sulphides as a source of sulphur are of considerable economic and technical interest, particularly to developing countries having ore deposits. Many non-ferrous ores occur as sulphides and require roasting in air before further smelting is possible to produce the metals. All these processes give rise to large quantities of gases containing SO_2 which used to be vented to atmosphere; this is still the practice in some parts of the world. However the effect of SO_2 in the atmosphere on vegetation was so deleterious that large areas of countryside were virtually laid waste by some of these earlier operations and restrictions have been imposed in most countries. Comparatively simple processes exist for absorbing the noxious gases but these generally are expensive to operate and give rise to large volumes of liquid effluents which may be nearly as

objectionable as the gases. Consequently, the practice of turning these SO_2 containing gases into a valuable industrial raw material was introduced and today, except in desert areas remote from population centres, the production of sulphuric acid is regarded as an essential part of these metallurgical operations.

4. The use of further alternative sulphur bearing raw materials may well be encouraged by many developing countries due to shortage of foreign exchange and in an effort to achieve economic self sufficiency regardless of the higher cost of acid thus produced from indigenous sources.

For example

(a) the process for making cement and sulphuric acid from calcium sulphate was developed in Germany during the First World War and the anhydrite process is still used in Britain.

(b) there is an increasing potential in hydrogen sulphide, particularly from petroleum refining and natural gas purification; it may, however, be more economic to make sulphur under some circumstances.

(c) "spent oxide" from the purification of carbonisation gases is often roasted for its sulphur content and the residual cinder value: this is likely to be a declining source since alternative processes for the purification of gas have been developed which either produce sulphur directly, convert the sulphur to an innocuous effluent, or produce sulphur dioxide gas which can be utilised in an acid plant.

(d) ferrous sulphate, produced in large quantities in the titanium dioxide pigment industry and in the pickling of iron and steel is also a possible alternative source.

5. The production of sulphuric acid from sulphur is in essence a very simple process.

(a) Sulphur is burnt in the presence of atmospheric oxygen to give SO_2 which then combines with further oxygen to give SO_3 gas in accordance with the following equations :

$$S + O_2 = SO_2$$

$$SO_2 + \tfrac{1}{2} O_2 = SO_3$$

$$SO_3 + H_2O = H_2SO_4$$

The reaction of SO_2 and oxygen is very slow and all commercial processes use a catalyst. The only catalysts of economic importance today, except under very exceptional circumstances, are based upon vandium pentoxide.

(b) Owing to considerations of chemical kinetics and equilibrium it is necessary to cool the SO_2 gas, before entering the catalyst beds, to a temperature of about 420°C and to abstract heat from the gas during the course of reaction. This heat may, together with that of the combustion of the sulphur either be rejected to atmosphere or recovered in the form of waste heat steam. Normally, except on very small plants it is economic to recover the heat and, even if no specific use for steam exists, it can be used to drive some of the machinery

on the plant. Indeed it is possible for the value of the steam on a large plant to very nearly pay for all the depreciation, labour, maintenance and services required by the plant so that the acid is obtained for very little more than the cost of the sulphur content.

(c) The sulphur trioxide formed cannot be absorbed directly in water because, as is well-known, it forms a very stable sulphuric acid mist under these conditions which is very difficult to recover, and it gives rise to atmospheric pollution. For the same reason, it is necessary to dry the air before the combustion of the sulphur. This is achieved on the plant by circulating some of the acid over a packed tower. A very much simplified flowsheet of a sulphur burning plant is shown in Figure I.

6. The production of acid from all the other sources mentioned is more complicated because the gases from most such sources cannot be treated in such a simple manner. Firstly, they generally contain appreciable quantities of dust which would plug the catalyst beds very rapidly and make the plant completely inoperable. Secondly, they may well contain some impurities which, while not harming the modern catalyst may temporarily reduce conversion efficiency and also contaminate the product acid. Consequently the methods of production of SO_2 containing gas, its purification and cooling, as mentioned below, have been developed. Furthermore, as the purified gas is then cold it has to be heated by heat exchange with the converted gas to give suitable operating temperatures in the converter. Some of the necessary unit operations are shown on the simplified flowsheet Figure II.

(a) The methods of production of SO_2 containing gases include

(i) at least four important different systems of pyrites roasting, and the actual selection in any particular case requires a careful balance of the conflicting requirements of gas strength produced, cinder quality, and production rate per unit: in all cases the ore is oxidised in atmospheric air at elevated temperature.

(ii) production from calcium sulphate in a cement-type rotary kiln for reduction of the sulphate by carbonaceous matter in the presence of an acidic oxide to combine with the calcium. It is, however, complicated by the economic necessity to produce an acceptable quality of cement simultaneously: this involves very careful blending of the raw materials and control of the firing conditions.

(iii) production from spent oxide in roasters of similar design to those used for pyrites but conditions are different and differences in detail occur.

(iv) production from hydrogen sulphide containing gases by simple combustion in air.

(v) ferrous sulphate reduction at high temperature by suitable fuel such as coal or oil, but there are complications due to the high moisture content of the gas both from combustion of the fuel and from the water of crystallisation of the ferrous sulphate.

(b) The primary product of the combustion of all these materials is a hot SO_2 containing gas which contains water vapour and generally, except in the case of H_2S burning, dust in suspension. Before use in a contact sulphuric acid plant the gases must be cleaned of dust to a very high degree of perfection. It is then necessary to dry the gases to a very low water vapour content before admission to the acid plant proper.

(i) dust removal is usually effected by the aid of cyclones and electrostatic dust precipitators which will normally recover 90 to 98% of the dust present. The degree of cleanliness required for a contact plant is, however, several orders of magnitude higher than this and the normal practice is to follow the primary purification with a wet washing system which cools the gases to a temperature in the order of 40°C. This process, however, does generate sulphuric acid mist arising from the small quantities of sulphur trioxide which are always found in the gases from the roasters and furthermore there are often metallic fumes present which, being in the vapour state, are not removed by the dust precipitators but are condensed (but only partly removed) in the washing system.

(ii) the removing of the acid mist and metallic fumes requires wet electrostatic precipitators which can clean to a very high degree of efficiency. The normal specification of the gas leaving the wet precipitator is that it shall be optically clear at a distance of several metres, and detection of impurities requires the most refined analytical methods.

(iii) in special circumstances an acceptable method of cleaning the hot gas and achieving the cooling in one operation can be achieved by using various types of impingement scrubber.

(d) An exceptional case is the modern wet catalysis process which is generally only suitable for treating H_2S gas which is free of all suspended solids. Under these circumstances, by the adoption of special techniques it is possible to dispense with the drying of the combustion air. Such plants, however, at the moment, only produce comparatively weak sulphuric acid which is acceptable for many purposes. Modern developments, however, open the possibility of producing concentrated acid, (about 92-95% strength) from such plants and it is anticipated that in the near future, such plants may be generally available.

7. Technically, it is possible to construct sulphur burning sulphuric acid plants of capacities of from less than 10 tons per day up to well over 1,000 tons per day, substantially in single stream units. This is not always true for other raw materials: for example it is doubtful whether the cement sulphuric acid process could be made to operate technically in capacities much under 50 tons per day.

TABLE I.

PRODUCTION COSTS OF SULPHURIC ACID

Showing variation with plant size and raw material.

Raw Material	Sulphur			Pyrites		Calcium Sulphate	
Capacity tons per day	25	100	500	100	500	100	500
Debits							
Raw Materials	74	74	74	75	75	65	65
Services	4	4	4	8	8	16.5	16.5
Maintenance	9	8	5	15	12	24	24
Labour	2	1	0.2	2	0.5	6.5	6.5
Fixed Charges	26	13	8	30	20	60	48
	115	100	91.2	130	115.5	172	160
Credits							
Steam	15	20	20.0	18	18		
By Products				24	24	80	80
Net Cost	100	80	71.2	88	73.5	92	80

All costs are based on U.K. values and given in shillings per metric ton of 100% sulphuric acid, and exclude all factory overheads.

8. Table I shows the economic problems inherent in the fixed charges on small plant. In the U.K. it is normally uneconomic to operate sulphur burning acid plants of less than about 50 tons per day or pyrites burning plants of less than 100 tons per day.

   The table also shows the substantial increase in fixed charges for two alternative raw materials, pyrites and calcium sulphate. It is also apparent that running below rated capacity (when the fixed charges increase per ton of product) is least important with sulphur as raw material.

9. In less developed countries the economics of small plants are much more attractive.

   (a) Many sulphur burning plants of the 10 ton per day size have been built which can operate economically at this rating and even lower.

   (b) Pyrites burning plants also have been built on the scale of 10 tons per day and can run economically if the raw material is available locally. Only under very exceptional circumstances is it economic to build plants of much lower capacity although these are technically feasible.

(c) Unfortunately the demand for very small plants is so low that the design costs incurred in the building represent a very substantial proportion of the initial cost and consequently, the price of a 5 tons per day plant would be nearly as great as 10 tons per day plant. It might even be higher, as most suppliers of such equipment have standard designs available for the 10 ton plant.

10. While the basic principles of sulphuric acid production have been the same for many years, continual research and development by manufacturers of these plants have reduced the costs in terms of a constant value of money very considerably. These developments involve improvements in the process design and in the application of the latest techniques in gas cooling and cleaning, and today, sulphuric acid can be made from almost any sulphur-bearing material by processes which are amply proved in commercial production. This experience and techniques are freely available to all parts of the world and should allow developing countries to make the best use of their available resources.

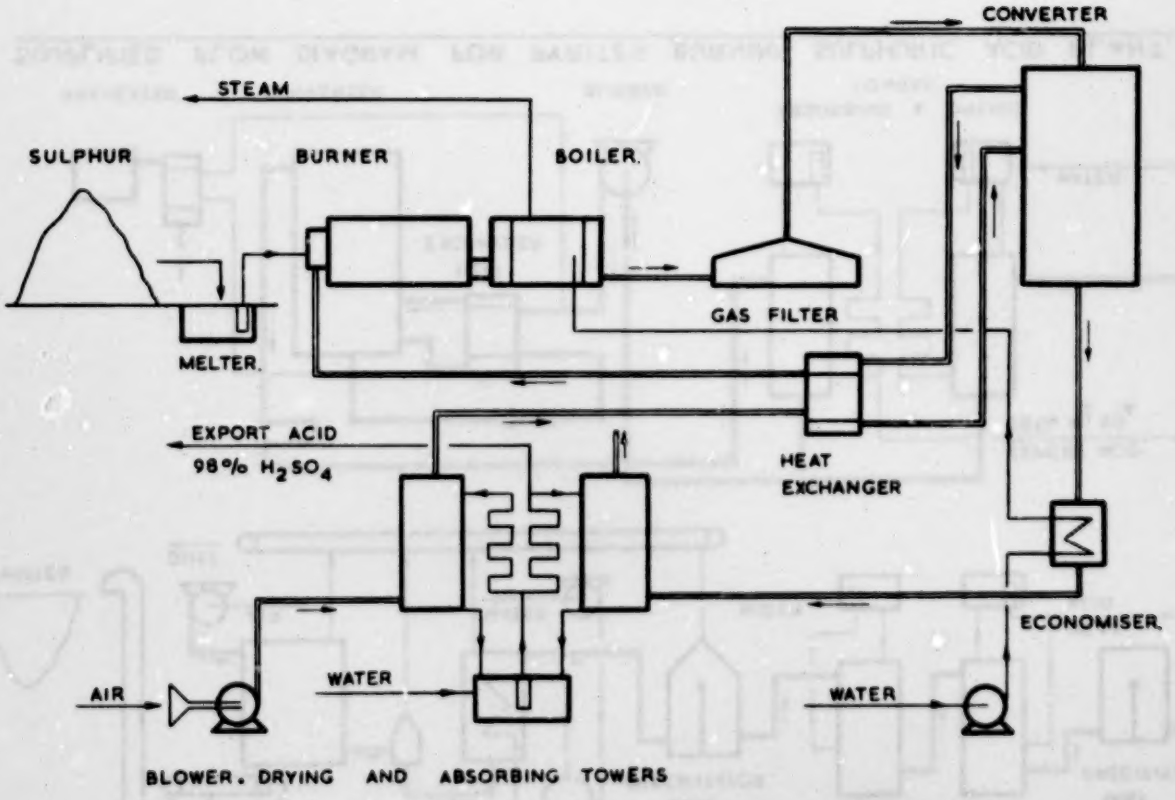

FIGURE I

SIMPLIFIED FLOW DIAGRAM FOR SULPHUR BURNING SULPHURIC ACID PLANT.

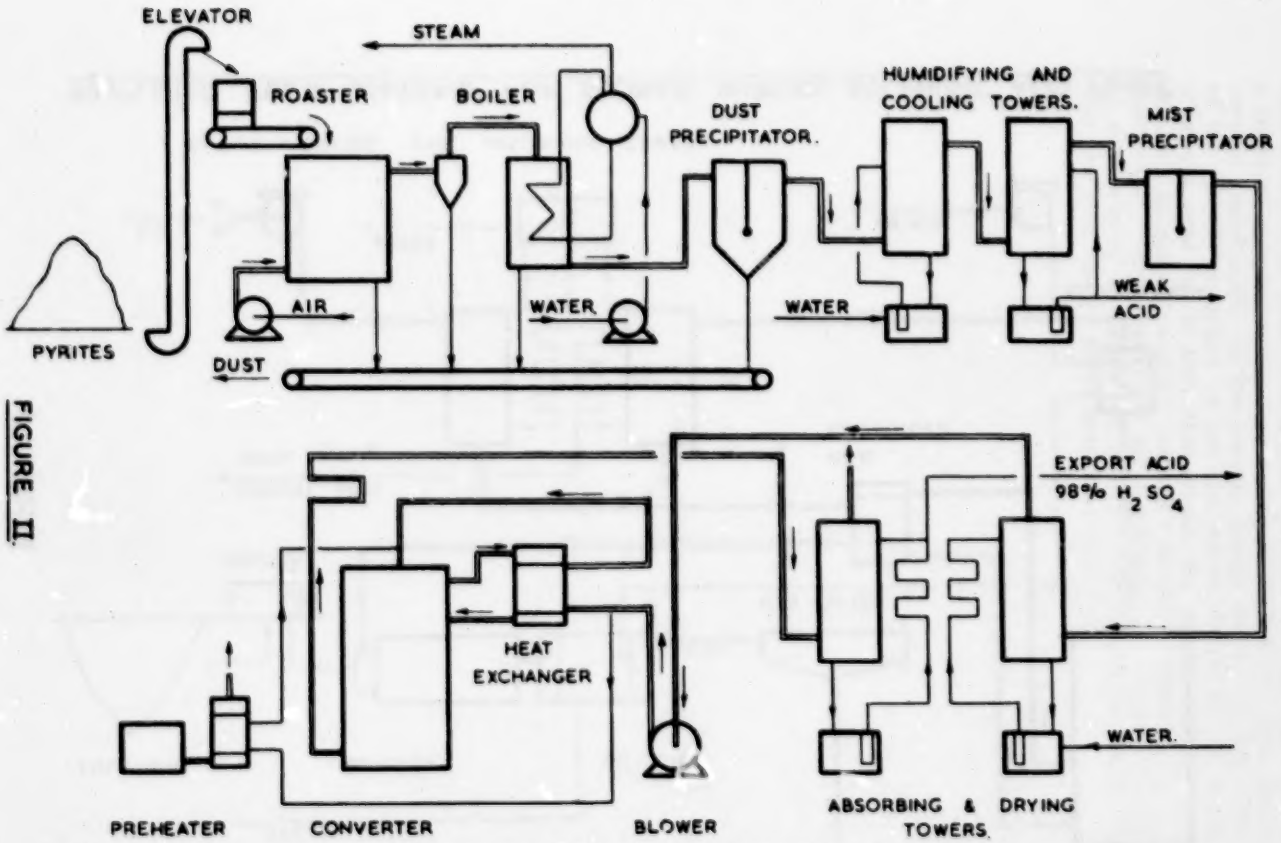

FIGURE II.

SIMPLIFIED FLOW DIAGRAM FOR PYRITES BURNING SULPHURIC ACID PLANT.

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